

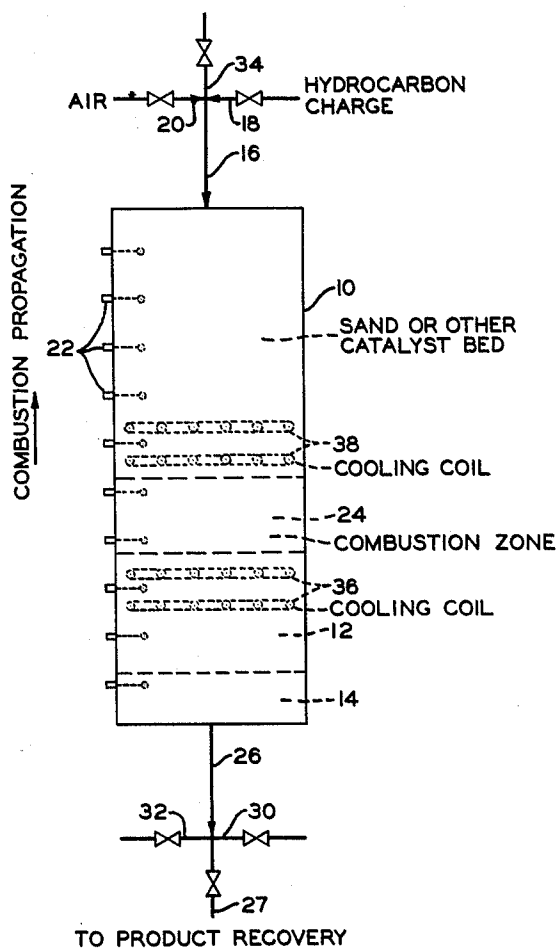
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J. C. TRANTHAM ETAL

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PROCESS FOR CONVERSION OF HYDROCARBONS

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INVENTORS.

J. C. TRANTHAM

C. J. ENGLE

BY A. R. SCHLEICHER

Hudson & Young

ATTORNEYS

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PROCESS FOR CONVERSION OF HYDROCARBONS
Joseph C. Trantham and Charles J. Engle, Bartlesville,
Okla., and Arthur R. Schleicher, Champaign, Ill., as-
signors to Phillips Petroleum Company, a corporation
of Delaware

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This invention relates to an improved process for the
conversion of hydrocarbons to more desirable products.

In conventional refining processes the hydrocarbon feed
is either preheated and passed over a catalyst or con-
tacted with hot catalyst in a fluidized bed. In either
case, the feed and/or catalyst are heated by means of
heat exchangers and do not actually come into intimate
contact with any combustion process. In catalytic re-
fining processes and in processes involving the synthesis
and production of complex organic compounds, the cost
of catalytic converters and heat exchange equipment adds
considerably to the cost of the processes. This inven-
tion is concerned primarily with a more economical and
improved method or process for the conversion of hy-
drocarbons to more valuable hydrocarbons and to com-
plex organic compounds, such as oxygenated hydrocar-
bons and other oxygenated products.

Accordingly, the principal object of the invention is
to provide an improved process for the conversion of
hydrocarbon materials to more desirable products. An-
other object is to provide an improved process for up-
grading and refining hydrocarbon materials. A further
object is to provide an efficient process for converting
crude oil to lighter hydrocarbon materials including gaso-
line boiling range hydrocarbons. It is also an object
of the invention to provide a process for the conversion
of hydrocarbons found in crude oil to azulene. Other
objects of the invention will become apparent to one
skilled in the art upon consideration of the accompany-
ing disclosure.

A broad aspect of the invention comprises mixing a
suitable hydrocarbon feed with air or other oxidizing gas,
such as diluted air, O₂-enriched air, or substantially pure
oxygen, and introducing the mixture into a combustion
zone in a porous or permeable bed of particulate re-
fractory solids, preferably one with catalytic properties.
A minor proportion of the hydrocarbon material is con-
sumed by the combustion by regulating the proportion
of oxygen in the mixture so as to maintain the desired
temperature in the combustion zone of the bed. Com-
bustion temperatures are preferably maintained in the
range of 900 to 1200° F., as these have been found to
be highly efficient in laboratory scale combustion tests.
The combustion consumes a minor proportion of the
hydrocarbon material and the remainder is cracked and
converted to lighter molecular weight hydrocarbons and
oxygenated compounds. The produced liquids and gases
are separated by conventional methods.

The hydrocarbon feed may comprise practically any
hydrocarbon material. Even normally gaseous hydro-
carbons may be converted to ethylene, acetylene, and
oxygenated products in accordance with the invention.
Generally speaking, subjecting a straight chain aliphatic
hydrocarbon to thermal cracking merely results in break-
ing the molecule up into fragments consisting principally
of lower molecular weight olefinic and aliphatic hydro-
carbons. We have found in tests that by charging a
substance such as n-cetane in admixture with air to a
sand-packed column in which a combustion zone is main-
tained, other products can be obtained. In one such
test, using 292 grams of n-cetane on Torpedo sandstone
in an inverse burning process, the products included a
blue liquid material identified as a concentrate of azulene,

which is a blue solid melting at 99° C. Azulene is an
isomer of naphthalene and has the formula C₁₀H₈. It
is the parent substance of a group of coloring matters
obtained from certain essential oils by oxidation. In
addition, other higher molecular weight substances in-
cluding aromatic hydrocarbons and their oxygenated
products were produced. Azulene was also produced in
an inverse in situ combustion of a tar sand in field oper-
ations.

Laboratory tests in which heavy crude oils and tars
were partially combusted in a bed of silica show that
the process greatly reduces viscosity and molecular weight
of the oils. The sulfur content of the effluent product
was greatly reduced and a large proportion of the product
is in the gasoline and gas oil ranges.

A more complete understanding of the invention may
be had by reference to the accompanying schematic
drawing in which numeral 10 designates a reaction ves-
sel or catalyst case which is packed with a permeable
bed 12 comprising solid particulate refractory material
which is preferably catalytic with respect to hydrocar-
bons. Silica in the form of sand, activated clay (alu-
minum silicate) synthetic silica, synthetic silica-alumina,
synthetic alumina, activated bauxite, and such materials,
alone or having other catalytic materials deposited there-
on are suitable for use as the permeable bed. Catalytic
material which can be incorporated in the bed include
the iron group metals (Ni, Co, Fe) and their oxides.
Cu, Mn, Mo, Cr, U, and V and their oxides are also
suitable for including in the catalytic materials in minor
amounts, such as 0.15 to 10 weight percent.

Reactor 10 may be a high temperature alloy vessel
or a carbon steel vessel provided with a refractory brick
lining.

According to one aspect of the invention a section
of the bed designated 14 is heated to combustion sup-
porting temperature by any suitable means such as burn-
ing therein a combustible mixture of gaseous hydrocar-
bon (propane) and air injected through line 16 and
ignited as it reaches the opposite end of the bed in sec-
tion 14. The hydrocarbon feed may also be the feed
to be converted. When section 14 has been raised to
combustion supporting temperature such as a tempera-
ture of at least 600 or 700° F., the feed to be converted
is introduced through line 18 and admixed with air in-
troduced through line 20, the air being of lesser propor-
tion than that required for complete combustion of the
hydrocarbon feed. The mixture passes through line 16
and through the bed 12 so that it is burned in section
14. Continuous burning of a portion of a hydrocarbon
in section 14 with regulation of the proportion of air
in the mixture causes the combustion zone to move to-
ward the opposite end of the packed bed. By position-
ing thermocouples 22 at spaced intervals along the bed,
the location of the combustion zone can be observed
at any time. When combustion zone 24 arrives at the
position shown in the drawing, it can be stabilized in
this area by proper regulation of the flow rate of air
and/or fuel into the bed. Effluent products are recovered
from the reactor through lines 26 and 27 and are passed
to product recovery means not shown.

The rate of air injection for any given feed injection
rate can be varied to move the combustion zone by direct
drive (concurrently with the feed) or by inverse drive
(countercurrently to the flow of feed). High flow rates
of air result in moving the burning zone by direct drive
while low flow rates of air move the burning zone in-
versely to the flow of feed. The rates of flow required
can be determined for each feed by observation of thermo-
couples 23.

Another aspect of the invention comprises continuing
the injection of the combustible mixture of hydrocarbon

and air through line 16 at such a rate of air flow and proportion of air to hydrocarbon as to cause the combustion zone 24 to move completely through the bed countercurrently to the flow of combustible mixture and, when the combustion zone arrives at the injection end of the bed, terminating the flow of the mixture through line 16 and then injecting hydrocarbon feed through line 30 and air through line 32 in such proportions that combustion zone 24 reverses itself and moves toward the opposite end of the bed inversely to flow of said feed. In this embodiment of the invention, it is usually necessary to inject liquid feed into the bed at reversal as it has the effect of cooling the bed in the injected end so that combustion is not immediately effected therein. In this manner, the feed (air and hydrocarbon) is raised in temperature as it moves through the bed until it reaches the hottest part thereof at the opposite end from the injection end. After cooling the major portion of the bed down by injection of the hydrocarbon feed in liquid form, the hydrocarbon feed is then injected in vapor form by preheating or vaporizing the feed in a heat exchanger not shown. During the reverse burning, the effluent products are recovered through lines 16 and 34 and the burning zone is progressively moved to the injection end of the bed. The cycle of passing the combustion front back and forth through the permeable bed is then repeated.

In accordance with another embodiment of the invention, the combustion zone may be positioned as shown in the drawing in accordance with the foregoing procedure and after this has been effected, a coolant is circulated through cooling coils 36 and 38. (These cooling coils are not incorporated in the bed when this embodiment of the invention is not to be used.) Circulation of coolant through coils 36 and 38 by means well known in the art prevents the refractory material surrounding the coil from heating sufficiently to permit the movement of a combustion front or zone through the cool material. In this manner the combustion zone is restricted to a well defined area intermediate the cooling coils.

The following examples are presented to illustrate the invention and are not to be construed as unnecessarily limiting the same.

Example I

A sand pack in a 2" stainless steel combustion tube containing 2919 g. of Barnsdall Sand was impregnated with 10 percent by weight n-cetane. The porosity of the pack was 41.7%, and cetane saturation was 54.3%. The original gas permeability was 2.8 darcys. It was ignited by counterflow technique (i.e., heated to 1000° F. at the sand face and then air was injected from the opposite end of the tube) and was burned countercurrently at an air flux of 300 s.c.f./hr./ft.². The combustion temperature averaged about 1050° F. at this air flow rate, the CO₂ content of the exhaust gas was about 12% and the CO content was around 1.9%.

Distillation of the liquid product gave 19.5% by volume of material boiling below cetane (287.5° C.). From this cut a small amount of a blue compound identified as azulene was separated by silica gel chromatography. Gas chromatography showed the presence of about 8 percent of the various 1-olefins from C₇ to C₁₂.

Example of combustion where location of combustion zone was controlled by regulation of fuel feed rate:

Example II

A 2-inch stainless steel tube, equipped with thermocouples TC₁-TC₂ was packed with clean, unconsolidated, round-grain sand ("spittoon sand") and it was flooded with North Burbank Unit oil (about 38° API gravity) until saturated. The excess oil was then swept out with air until the oil came out as occasional drops. Because of previous difficulties in igniting oil of this high gravity either by cocurrent or countercurrent air flow a section of approximately 2 inches of Clear Creek Tar Sand was

packed adjacent the electrical igniter and this tar sand was ignited by heating to 580° F. at TC₁ in a stream of nitrogen and then passing air cocurrently at 340 s.c.f./hr./ft.² through the heated tar sand. When the fire front approached the discontinuity between the tar sand and the oil-saturated sand, the air flow was reversed. The combustion continued by countercurrent burning and the temperature at TC₂ rose rapidly to 1300° F. It then rose gradually to a maximum at 1800° F. At this point, the air flux was reduced to 183 s.c.f./hr./ft.² and the temperature at TC₂ went through another maximum at 1480° F. The behavior of the temperature at TC₂ indicated that the higher air flux prevailing immediately after the air direction was reversed moved too much of the liquid fuel into the fire zone and drove it back towards TC₁. Thus TC₂ went through a maximum as the fire front passed it moving in the direction of the air flow. When the air flux was reduced, liquid fuel was allowed to remain in place while air was fed to the fire zone. This caused the fire to burn countercurrently past TC₂ (resulting in a second maximum) seeking fuel. The second maximum was broad, indicating a slow movement of the fire zone. Since the direction of movement was varied at will by varying the air flux, an air flux can be found which will maintain the fire zone stationary during countercurrent burning.

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

We claim:

1. A process for upgrading and converting hydrocarbons to more desirable products which comprises providing a stationary particulate elongated bed of solid refractory material within an elongated reaction chamber occupying substantially the entire reaction zone therein; heating a complete transverse cross section of said bed at one end thereof to combustion-supporting temperature; forming a mixture of said hydrocarbons and air in which the air concentration is substantially less than that required for complete combustion of said hydrocarbons and at a temperature below combustion temperature; thereafter passing said mixture into the hot section of said bed so as to ignite same and establish a combustion zone throughout said cross section, thereby burning a substantial proportion of said hydrocarbons so as to maintain the temperature of said zone in the range of 900° to 1200° F. and convert within said bed a substantial proportion to lighter hydrocarbons and oxygenated products; regulating the flow rate of said mixture and the proportion of air therein so as to move a relatively thin combustion zone through said bed toward the opposite end thereof; and recovering said hydrocarbons and products from one end of said bed.

2. The process of claim 1 wherein said combustion zone is moved to a section of said bed intermediate its ends and maintained there by regulating the flow rate of said mixture and the proportion of air therein, and products are recovered from the opposite end of said bed.

3. The process of claim 2 wherein said mixture is passed through said bed from the ignited end and said zone is caused to move into said intermediate section by controlling the rate of flow of air in relation to the rate of flow of hydrocarbons in said feed.

4. A process for the conversion of hydrocarbons which comprises establishing a hot zone at a temperature above combustion temperature of said hydrocarbons in one end of an elongated permeable stationary bed of particulate solid refractory material occupying substantially the entire reaction zone in a reaction chamber; forming a combustible mixture of hydrocarbons and air outside of said bed at a temperature below combustion temperature and passing same through said bed from the other end into said zone, said air being substantially less than that required for complete combustion of the hydrocarbons in

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said mixture so as to establish a combustion zone and burn a substantial proportion of said hydrocarbons and convert a substantial proportion to other hydrocarbons and oxygenated products; regulating the ratio of air to hydrocarbons in said mixture so as to cause said combustion zone to travel through said bed to said other end; and recovering products from said one end.

5. The process of claim 4 including the steps of changing the flow of said mixture into said bed to said one end when said combustion zone arrives adjacent said other end, thereby causing the combustion zone to reverse through said bed to said one end, and recovering products from said other end during the reverse travel of said zone.

6. The process of claim 1 wherein said bed comprises a conversion catalyst.

7. The process of claim 1 wherein said bed comprises a cracking catalyst.

8. The process of claim 7 wherein said catalyst comprises silica.

9. The process of claim 7 wherein said catalyst comprises silica and an iron group metal oxide.

10. The process of claim 7 wherein said catalyst comprises silica-alumina.

11. The process of claim 1 wherein said combustion zone is moved to and maintained in an intermediate section of said bed by circulating a coolant through a transverse section of said bed in indirect heat exchange therewith on each side of said combustion zone.

12. The process of claim 1 wherein said feed is a crude oil.

13. The process of claim 1 wherein said feed is a gas oil.

14. The process of claim 1 wherein said feed is a gasoline boiling range stock.

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15. The process of claim 1 wherein said hydrocarbons include n-cetane and azulene is produced and recovered.

16. A process for converting hydrocarbons to more desirable products which comprises packing an elongated bed of particulate refractory solids into a reaction zone so that said bed occupies substantially the entire reaction zone; saturating said bed with a hydrocarbon oil; igniting one end of said bed by heating same to above ignition temperature of said oil and injecting air free of fuel into the heated area; continuing the injection of fuel-free air so as to burn a substantial portion of the oil and convert within said bed a remaining portion of said oil to lighter hydrocarbons and oxygenated products; and recovering the converted hydrocarbons from said bed.

17. The process of claim 16 wherein said oil is a high gravity oil which is difficult to ignite and ignition is effected by packing a tar sand into the ignition end of said bed, heating said sand to above ignition temperature, injecting air into the ignited sand from said ignition end so as to burn through to the inner end of the tar sand pack, and thereafter reversing the flow of air so that it enters the opposite end of said bed.

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